

Review of “Measurement of the ambient organic aerosol volatility distribution: application during the Finokalia Aerosol Measurement Experiment (FAME-2008)” by Lee et al., Atmos. Chem. Phys. Discuss., 10, 17435–17466, 2010.

Lee et al. present measurements from the FAME-2008 campaign of ambient OA mass loadings and how the OA mass changes as the particles are passed through a thermodenuder (TD) maintained at elevated temperatures. An interesting contribution from this paper is the measurement of mass thermograms for different TD residence times (14 sec and 105 sec). Their results clearly indicate that the particles do not achieve equilibrium in the TD within 14 seconds, indicating that a non-equilibrium model must be used to interpret the observations. However, only a few data points at the longer residence time were measured, which, in my opinion, limits the consideration of these longer residence time results to be qualitative. My overall opinion is that the conclusions are not completely justified by the presented analysis and tend to overstate the case that can actually be made in many places. As with Reviewer #1, I believe that significant revisions to this manuscript will be necessary before it can be considered for publication. However, I do think that ACP could be an appropriate venue despite the relatively heavy “technical” side to the paper, so long as revisions are made to emphasize and clarify the “science”.

General: The vast majority of the measurements were made over a very limited temperature range (ca. 100-115°C). The authors should explicitly comment on why such a limited temperature range was considered. Other recent ambient TD/AMS measurements have generally taken the approach of using temperature ramps in order to allow for measurement of mass thermograms with data points that span a much larger temperature range. The temperature ramp method effectively provides greater information content than when a narrow temperature range is considered, as was done here.

p. 17442-20: The authors put forth a correction scheme that can be used to determine changes in particle collection efficiency in the AMS upon heating of the particles. They state that the CE is 85% for ambient particles but that this decreases to 76% for denuded particles (it is not stated at what temperature this was determined). Following this, they state that “After application of this collection efficiency, the AMS sulfate concentration agreed well ( $R^2 = 0.95$ ) with concentrations measured independently by PM 1.3 filters (Hildebrandt et al., 2010) during the full duration of the study. This agreement increases our confidence in the estimated CE values.” It seems only fair to also mention that the same comparison was done for OA by Hildebrandt et al., with a somewhat lower  $R^2$  value (0.78), although it is possible that some of the additional scatter in the OA arises. It should also be made clear that it is only the *ambient*, and not the denuded, measurements where the AMS mass was compared with filter based measurements. As such, I do not see how this comparison provides confidence in the results for the derived thermodenuded CE. Finally, can the authors comment further on the comparison between the AMS and filter results given that the filter results were for  $PM_{1.3}$  while the AMS is only sensitive to particles less than  $\sim 1 \mu m$ ?

p. 17442 and Figure 2: Since an AMS was used behind the TD the authors were also able to measure sulfate concentrations. Was there any loss of sulfate through the thermodenuder (i.e. did the MFR for sulfate decrease below 1)? If so, can the authors comment as to what extent this might have influenced

the collection efficiency? In other words, is it possible that the deduced changes in CE resulted from changes in sulfate and not organics alone?

p. 17442 and Figure 2: Can the authors comment more specifically on the difference between the CE values determined for this study and the typically assumed value of 0.5 (see Canagaratna et al., 2007), especially given that the particle mass was dominated by sulfate? At minimum, a reference to Hildebrandt et al. (2010) seems necessary since this is discussed to some extent in that paper.

p. 17442-24: At what temperature was the average density for the denuded particles determined? I assume 110°C, although measurements were made up to 140°C?

p. 17443-6: The authors state that the CE results are relatively insensitive to their treatment of particle water. However, I would assume that most of the water is removed from the denuded particles prior to measurement in the AMS. As such, the denuded and ambient particles may have very different water contents. It is stated that if it is assumed that the particles lose half their water in the AMS inlet then the CE changes by less than 5%. However, if the ambient particles contain water but the denuded particles have no water then the same assumption as to particle water should not be made for the denuded and ambient particles. How would this affect the CE results? Can I assume that if loss of half the water leads to a 5% change in the estimated CE then loss of all the water would lead to a 10% change? A change in the thermodenuded CE by 10% would be large enough to bring it into agreement with the non-denuded CE. However, related to this, if particle phase water is indeed removed in the TD (which I believe it would be), wouldn't one expect the decrease in CE to be greater than was observed since it was argued in Hildebrandt et al. (2010) that the reason for the "high" collection efficiency ("high" meaning > 0.5; Canagaratna et al., 2007) was that the particles contained enough water so as to be liquid? Also, since it is stated that particle water ranged from 0-20%, shouldn't periods of low CE have been observed when low particle water was observed?

p. 17443-25: I find the discussion of the particle number loss to be insufficient with respect to the treatment of temperature dependent losses. The authors report only one value for the particle loss through the TD (15%), but do not report the temperature to which this corresponds. They state that the fractional loss is temperature dependent, but do not state how they account for this temperature dependence. Since they do not show a figure they must at minimum report the equation that they use to determine the temperature dependent losses. Furthermore, it appears that this loss rate was determined by plotting the particle number concentration from the TD vs. ambient and determining the slope (Figure 3). Implicit in this methodology is the assumption that the particles are internally mixed. If the particles were externally mixed to any extent then it is entirely possible that some particles could evaporate entirely whereas others will persist in the TD. This implicit assumption should be stated and, if the data exists (such as can be obtained from single particle measurements), justified by observations. If some particles do evaporate entirely as they transit the TD, they are removed from the distribution, but this is not really a "loss" in the sense that it is used here. As such, the 15% would seem to be an upper limit. Also, is the particle loss the same at the 14 sec residence time as it is at the 105 sec residence time? This is not stated.

p. 17444-6: Algorithm Consistency Check: It is not clear that this is indeed a “consistency” check. The CE and density values were determined based on a comparison between AMS and SMPS data and thus the results for one are not separable from the results of the other. As such, the results shown in Figures 4 and 5 do not seem to provide added confidence that the corrections are reasonable, only that that they were applied correctly. Similarly, the check provided in this section does not support the claim that the AMS and SMPS are consistent with each other. In fact, given that the AMS results were corrected using the SMPS results it would be surprising if the corrected values were not in agreement!

p. 17446-2: I believe that the continued references to the unpublished Lee et al. paper are not warranted given that this paper is not yet published. References to this unpublished manuscript should be minimized and the reference should be given as a footnote to make it clearer to the reader that they are referencing unpublished work.

p. 17446-12: The authors have selected as a base case to use  $\Delta H_{\text{vap}} = 80$  kJ/mol, which they state is “not far from the Saathoff et al. (2009) estimate for the less volatile  $\alpha$ -pinene SOA component.” However, Saathoff et al. actually report a value of 59 kJ/mol. It has been shown (Cappa, 2010) that TD models are particularly sensitive to the choice of  $\Delta H_{\text{vap}}$  for  $\Delta H_{\text{vap}}$  values of less than  $\sim 100$  kJ/mol, and therefore the difference of 21 kJ/mol between the base case here and the Saathoff et al. results could actually be considered as quite different, rather than “not far from.”

p. 17446-19: A reference to Saleh et al. (2009) should be included. Saleh et al. found that the effective mass accommodation coefficient for a few dicarboxylic acids was less than 1. Also, a reference to Grieshop et al. (2009) is needed, since they (somewhat strangely) found an effective mass accommodation coefficient for lubricating oil was much less than one. Associated with this, it is difficult to ascertain to what extent the 0.05 value for the mass accommodation coefficient is reasonable given that the Lee et al. (2010) paper is not published and that the papers by Grieshop (2007, 2009) suggest a much lower mass accommodation coefficient (0.001-0.01). Given the inherent uncertainty in the mass accommodation coefficient, I would argue that a better “base case” would be to use a value of 1 and to use alternate values as “other” cases. This suggestion is further justified by the finding that the data can be equally well fit using a mass accommodation coefficient of 0.05 or 1, just with basis-sets that vary over different volatility ranges. Thus, by using a value of 1 as a base-case all other mass accommodation coefficient cases can simply be understood as an equivalent increase in the  $C^*$  values of the bins in the basis-set.

Figure 6: It is easily understood why the corrected MFR is greater than the uncorrected MFR. However, it also appears in this figure that the thermodynamic temperature for each point has been shifted with the correction. It is not clear why this should be the case and seems to be a mistake.

p. 17448: OA Volatility Distribution: I find the use of three different basis sets to be confusing. It should be equivalent to use a single basis set that ranges from the lowest value,  $0.001 \mu\text{g}/\text{m}^3$ , to the highest value,  $100 \mu\text{g}/\text{m}^3$ , considered. This simply corresponds to having 6 bins instead of 4, with some of the factors set to zero. The use of a greater range of values in the volatility basis-set (i.e. more bins)

ultimately provides greater flexibility in the model and would (likely) result in the authors being able to fit the data well over a broader range of conditions.

p. 17448-11: In fitting their observations to the volatility model, the authors chose to give equal weight to the short (14s) and long (105s) residence time measurements, despite the fact that considerably more measurements were made at 14s. To achieve this, they replicated their 105s data to have an equal number of points as the 14s data. I believe that this procedure unfairly weights the 105s data and should not be done. It is my opinion that a more appropriate method would be to first fit one of the data sets (14s) and then to compare the calculated mass thermogram at 105s determined using the fit parameters to the observations. Further, consider that the variability in the 14s observations is fairly large around a given temperature. Therefore, one might ask if the three data points that make up the entirety of the 105s data set are really very robust. For example, the VFR for the single point at 130°C is greater than at 110°C, which is a physically unrealistic result. Therefore, the data fit should only be done on the 14s data or, if the authors insist on including the 105s data in their fit, only the three data points should be included (i.e. there should be no data replication).

Related to this is the actual fit to the observations. Visual inspection of Figure 7 suggests that the fit to the data is actually quite poor: the model fails to capture the majority to the data points at ~110°C, tending to give higher VFR results than were observed. Shouldn't a best fit to a model generally pass through the region where the majority of the data points are located, which in this case is in the 110°C region? I would guess that this inconsistency is likely a result of including the replicated 105s measurements in the fit (see the above point).

p. 17448: OA Volatility Distribution: No reference to the recent work by Cappa and Jimenez (2010) is given in this work. This is a significant oversight given that Cappa and Jimenez used a similar methodology to deduce volatility basis-set's for ambient aerosol (from the MILAGRO campaign). A reference to that paper is clearly needed and discussion of the results from this study in terms of the conclusions of that paper should be added. In this context, the statement on page 17438 that a "lack of the corresponding theoretical analysis" makes comparisons between different studies difficult should be revised. Cappa and Jimenez (2010) showed that it is possible to fit field observations to a similar volatility basis-set/evaporation model with a number of different assumptions regarding the enthalpy of vaporization. In order to fit the observations it was necessary to adjust the number of bins in the basis set, with more bins generally necessary for higher  $\Delta H_{\text{vap}}$  values. However, the important result was that the observations could be well matched to the model using many different assumptions as to the  $\Delta H_{\text{vap}}$ . The authors should comment on this previous finding in light of their model results, which only briefly investigated the influence of different choices of  $\Delta H_{\text{vap}}$  and used a limited number of bins (four) in the basis-set.

p. 17448-18: The authors conclude that "the observations can be explained with all the OA being semivolatile ( $C^* \geq 10^{-2} \mu\text{g}/\text{m}^3$ )." However, their TD measurements only go out to 140°C and thus do not provide firm constraints on the lower limit of the OA volatility. For example, it is possible (at least in theory) for the presented mass thermograms to flatten out at higher temperatures, thus necessitating ever lower volatility compounds. The authors need to be more specific by stating that at least e.g. ~60%

of the OA mass is semi-volatile (with the 60% figure derived from the minimum MFR for the 14 s results).

P. 17449-10: The authors state that the FAME-2008 aerosol is ca. 2 orders of magnitude less volatile than fresh laboratory-generated SOA from  $\alpha$ -pinene ozonolysis. A more precise statement would be that they determined that the FAME-2008 aerosol has some components that are 2 orders of magnitude lower than the lowest volatility components determined for the lab SOA (for the base case). This is different than stating that the aerosol itself is lower volatility by 2 orders of magnitude. However, to return to a previous point, the lowest volatility bin considered here is likely an upper limit, since the MFR measurements only go to MFR = 0.4 (for the 14 sec TD). Also, this is only true for the base case, which assumes a mass accommodation coefficient of 0.05. If the mass accommodation coefficient is assumed to be 1 then the volatility of these “low” volatility components will effectively be decreased and the apparent lab/ambient gap will grow. Further, this conclusion will change if a different value is assumed for the enthalpies of vaporization. If smaller  $\Delta H_{\text{vap}}$  values are assumed, the ambient aerosol will appear to be comprised of higher volatility components than if higher  $\Delta H_{\text{vap}}$  values are assumed. Thus, I believe that this particular conclusion is fraught with unstated caveats (this is one example of where I find the paper to overstate the case).

P17449-25: The authors state that assuming a  $\Delta H_{\text{vap}}$  value of 45 kJ/mol does not reproduce the measurements as well as if 80 kJ/mol is used (with an accommodation coefficient of 0.05). However, again I believe the replication of the 105s observations is driving this result. Looking at the fits in Figure 9, it seems clear that if only the 14s observations were included the 45 kJ/mol assumption could easily be used to give just as good a fit as the 80 kJ/mol assumption.

p. 17450-1: The authors find that it is not possible to fit the model to the observations when enthalpies estimated using an empirical relationship given by Epstein et al. (2010) are used. The difficulties in using this empirical relationship have previously been discussed by Cappa and Jimenez (2010) and arise from the rapidly increasing enthalpies of vaporization with decreasing vapor pressure. Given that one of the authors (Riipinen) was on the Epstein paper, and that the relationship given by Epstein is empirical (and therefore, in some ways, more physically plausible than the fixed 80 kJ/mol base case), further discussion of the problems associated with using the Epstein values seems warranted. It is my guess that the difficulties associated with using the Epstein relationship here are in part related to the discussion given in Cappa and Jimenez and in part related to the fact that a basis set was used that only spans 4 orders of magnitude. It is likely that, given enough bins in the basis set, the authors would be able to ultimately obtain a reasonably good fit to the data. This is an inherent limitation of use a pre-constrained number of bins for the volatility basis set.

p. 17451-8: The authors suggest that even longer residence times than 105 seconds may be needed to ultimately constrain the volatility of ambient OA from TD measurements. Can they comment on the experimental feasibility of going to such long residence times for field measurements?

General: As mentioned by reviewer #1, the assumption that reactions within the TD have not modified the aerosol properties (beyond evaporation, of course) should be stated along with appropriate references (e.g. Denkenberger, 2007).

Figure 10: I believe that this figure is unnecessary. The text on p. 17450-13 is sufficient to make the point, not to mention that the basis-set used for the  $\alpha = 1$  case is shifted one order of magnitude down from the  $\alpha = 0.05$  base case.

Figure 8 and 17449-6: The authors present sample volatility distributions for a total organic concentration of  $10 \mu\text{g}/\text{m}^3$  and for a total aerosol concentration of  $2.8 \mu\text{g}/\text{m}^3$ . It is easy to understand why the  $2.8 \mu\text{g}/\text{m}^3$  value was used (the average for the campaign), but more discussion is necessary in relation to the  $10 \mu\text{g}/\text{m}^3$  case, if it is to remain. I would actually recommend removing the  $10 \mu\text{g}/\text{m}^3$  case as it doesn't seem to add much to the discussion beyond the  $2.8 \mu\text{g}/\text{m}^3$  case (i.e. the distributions don't really look very different).

#### References:

Denkenberger, K. A., Moffet, R. C., Holecek, J. C., Rebotier, T. P., and Prather, K. A.: Real-Time, Single-Particle Measurements of Oligomers in Aged Ambient Aerosol Particles, *41*, 5439-5446, 10.1021/es070329l, 2007.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spectrometry Reviews*, *26*, 185-222, 2007.

Cappa, C. D., and Jimenez, J. L.: Quantitative estimates of the volatility of ambient organic aerosol, *Atmos. Chem. Phys.*, *10*, 5409-5424, 10.5194/acp-10-5409-2010, 2010.

Cappa, C. D.: A model of aerosol evaporation kinetics in a thermodenuder, *Atmos. Meas. Technol.*, *3*, 579-592, doi:10.5194/amt-3-579-2010, 2010.

Epstein, S., Riipinen, I., and Donahue, N. M.: A Semi-Empirical Correlation between Enthalpy of Vaporization and Saturation Concentration for Organic Aerosol, *Environ. Sci. Technol.*, *44*, 743-748, doi:10.1021/es902497z, 2010.

Saleh, R., Shihadeh, A., and Khlystov, A.: Determination of evaporation coefficients of semi-volatile organic aerosols using an integrated volume—tandem differential mobility analysis (IV-TDMA) method *J. Aerosol Sci.*, *40*, 1019-1029, doi: 10.1016/j.jaerosci.2009.09.008, 2009.

Grieshop, A. P., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Constraining the Volatility Distribution and Gas-Particle Partitioning of Combustion Aerosols Using Isothermal Dilution and Thermodenuder Measurements, *Environ. Sci. Technol.*, *43*, 4750-4756, 10.1021/es8032378, 2009.

Hildebrandt, L., Engelhart, G. J., Mohr, C., Kostenidou, E., Lanz, V. A., Bougiatioti, A., DeCarlo, P. F., Prevot, A. S. H., Baltensperger, U., Mihalopoulos, N., Donahue, N. M., and Pandis, S. N.: Aged organic

aerosol in the Eastern Mediterranean: the Finokalia Aerosol Measurement Experiment – 2008, 10, 4167-4186, 10.5194/acp-10-4167-2010, 2010.